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## EXTREME ULTRA-VIOLET SPECTRA

BY R. A. MILLIKAN AND I. S. BOWEN

### ABSTRACT

**Extreme ultra-violet spectra, to 136 Å, of twenty light elements, H to Cu.**—Using the vacuum apparatus and explosive spark previously described, many plates have been made with a great variety of electrodes. By measuring and comparing thirty of these, over 800 lines between 136 Å and 1862 Å have been identified as belonging to one or other of the twenty elements studied. For H(1) only two lines, members of the Lyman series, were found; for He(2), and Li(3) none, though carefully looked for; for Be(4) one doubtful weak line; for Na(11) one strong line  $\lambda 372.3$  and one doubtful one  $\lambda 376.6$ ; for the other elements B(5), C(6), N(7), O(8), F(9), Mg(12), Al(13), Si(14), P(15), S(16), Cl(17), K(19), Ca(20), Cr(24) and Cu(29) from 9 to 160 lines each, all given in Tables. The strongest lines for each of the light elements are *L series lines* and form a progression like Moseley's for x-ray lines: Li (red), Be 3131.19, B 2066.2, C 1335.0, N 1085.2, O 834.0, F 656.4, Na 372.3, Mg 231.6, Al 162.4. These are mainly doublets, the separation increasing regularly with atomic number. *M spectra* also extend to shorter wave-lengths the higher the atomic number, reaching about 155 Å for Cu, but on account of the complexity of the spectra only a few lines have been identified. *Other series lines* identified are: 2 diffuse series lines and 2 sharp series lines due to  $\text{Mg}^+$  or Mg(II), 5 lines due to  $\text{Al}^+$  and 9 due to  $\text{Al}^{++}$  or Al(III), 11 lines due to Si(IV) and probably the first terms of the principal series and of the diffuse series of P(V). *Interpretation in terms of Bohr theory.* By use of the Kossel equation in connection with available data it is shown that for Na, 372.3 Å corresponds to an electron jump from the M shell to L(I); for Mg, 320.9, and 323.2 and 231.6 correspond to  $\text{M(I)} \rightarrow \text{L(II)}$ ,  $\text{M(I)} \rightarrow \text{L(III)}$  and  $\text{M(III)} \rightarrow \text{L(I)}$ ; for Al, 162.4, 200.0, 230.8, 186.9 may correspond to jumps from shell 3 to the L shell; for Ca, 655.9 and 669.6 correspond to jumps  $\text{N(I)} \rightarrow \text{M(II)}$  and  $\text{N(I)} \rightarrow \text{M(III)}$ . These interpretations give values of *constants of the L and M levels of the atoms as follows*: For Na, L(I),  $\nu/R=2.826$ ; for Mg, L(I) 4.298, L(II) 3.402, L(III) 3.381; for Al, L(I) 6.045, L(II) L(III) 5.008. The square roots of these values are linear functions of the atomic number. For Ca M(II),  $\nu/R=1.839$ , M(III) 1.810. From the difference L(II)–L(III) for Mg, the *screening constant* comes out 3.1; from the difference M(III)–M(II) for Ca, the constant is 7. These results are all in good agreement with other data.

**Ionization produced by explosive spark in vacuum.**—The strongest spectrum lines are generally emitted by stripped atoms, that is atoms with no valence electrons left, Na(I), Mg(II), Al(III), Si(IV), P(V), etc.

A PRELIMINARY report has been made by one of us<sup>1</sup> upon the most conspicuous characteristics of the extreme ultra-violet spectra of the light elements from hydrogen up to aluminum (atomic numbers 1 to 13) as revealed by the work which pushed down to 136 Å the limits of the region of wave-lengths explored by grating methods.

Since that report was made a very prolonged and detailed study and comparison of a large number of plates taken with many different electrodes has been made. This study has involved a double measurement by the second of us of not less than 5000 lines and the comparison by both of us of the spectra found on 30 different plates taken with different electrodes for the sake of deciding what lines belong to each particular element. It is the results of that study which are presented herewith.

The apparatus and methods have been sufficiently described in preceding articles. Since our main object thus far has been the location of as many new lines as possible, we have, of course, sacrificed resolution to intensity, not using in general more than a fiftieth of our theoretical resolving power. For some of the studies in which we are now engaged we are using higher resolution.

As indicated in the preliminary report the key to the identification of lines was first found in the discovery that between 1000 Å and 330 Å chemically pure magnesium and aluminum gave practically identical spectra while on the same plates the lines above 1300 Å were all different and corresponded, the one to the well known spectrum of aluminum, the other to that of magnesium. This meant that the spectra on both plates below 1000 Å was the nearly pure spectrum of the oxygen atom, since no other impurity of importance could be present. This identification of the oxygen lines was checked by the fact that the oxygen spectrum appeared practically complete with the use of all oxidizable electrodes, diminishing in intensity as the electrodes became less and less oxidizable and disappearing entirely with silver.

Having thus the oxygen spectrum and knowing in this way that there were practically no aluminum lines between 1300 Å and 230 Å we could obtain the correct spectrum of carbon in this region by subtracting from the observed carbon spectrum the oxygen and aluminum lines since these were the only probable impurities in carbon.

An extension of the foregoing method to a large number of plates and electrodes, many of which were compounds, obviously involves not only painstaking work but also a very considerable exercise of judgment especially in the case of the very weak lines. In the following tables where we have felt that there was little or no uncertainty we have classed

<sup>1</sup> Millikan, Nat. Acad. Sci. Proc. 7, 289-294, Oct. 1921.

the line in question without comment under the element to which in our judgment it belongs. Where there was about equal probability that it belonged to either one of two elements, for example oxygen and sodium, we have listed it under both and have followed the figures representing the wave-length in each case by the symbol of the other element without other notation, thus:

Sodium	Oxygen
1345 O	1345 Na

To indicate a considerably greater probability that the line belongs to one rather than the other of the two elements in question it is also recorded under each but with a subscript 1 underneath the symbol of the element to which it is thought to belong and a subscript 2 underneath the symbol of the element to which it may, though with considerable improbability, belong. Thus in the following notation the weight is thrown on the oxygen and the probability that it belongs to sodium has been reduced.

Sodium	Oxygen
4567 O <sub>1</sub>	4567 Na <sub>2</sub>

In cases in which we feel much confidence that the line belongs to a given element but in which we wish to indicate a mere possibility that it belongs to another we list it under the first element alone but follow it by the symbol of the other element with the subscript 3. This notation is then our first stage of uncertainty.

Wave-lengths are given in I. A. units reduced to vacuum, the 1854.7 and 1862.7 aluminum lines being used as fundamental standards.

Wave-numbers are reciprocals of wave-length, the latter being carried in obtaining these reciprocals to two places of decimals although in the wave-length column but one decimal has been retained.

With this introduction we list the new lines which we have brought to light, something like a thousand in number, under their appropriate elements and follow each table with such comments as seem necessary.

#### HYDROGEN

The only hydrogen line which we get consistently on nearly all plates is the first member of the Lyman series at 1215.7 Å. It is significant, however, that we have taken plates with certain electrodes, notably thallium, cadmium, and lead, without getting any trace of this line. This is excellent evidence that the hydrogen does not come from residual gases, from stopcock grease, or from the walls of the vessel, but rather from the electrodes themselves. It makes it probable too that it is not due to hydrogen gas or water vapor occluded in the electrodes since these

gases should be occluded in, or condensed upon, these three electrodes as much as upon others. It is significant also that although the line at 1215.7 Å appears in intensity as high as 5, 6, and 7 on certain plates we have observed none of the other members of this series except the second, namely 1025.6 Å and this has occurred in intensity 0 on but five out of thirty plates.

TABLE I

Int.	<i>Hydrogen</i> $\lambda$	$\nu$
0	1025.6	97507
4	1215.7	82254

TABLE II

Int.	<i>Beryllium</i> $\lambda$	$\nu$
3	1512.8	66102

## HELIUM

No trace of any helium line of the ultra-violet series has ever been found in any of this work with metallic electrodes. We have looked carefully for the first member of the helium ultra-violet series beginning at 1640 Å

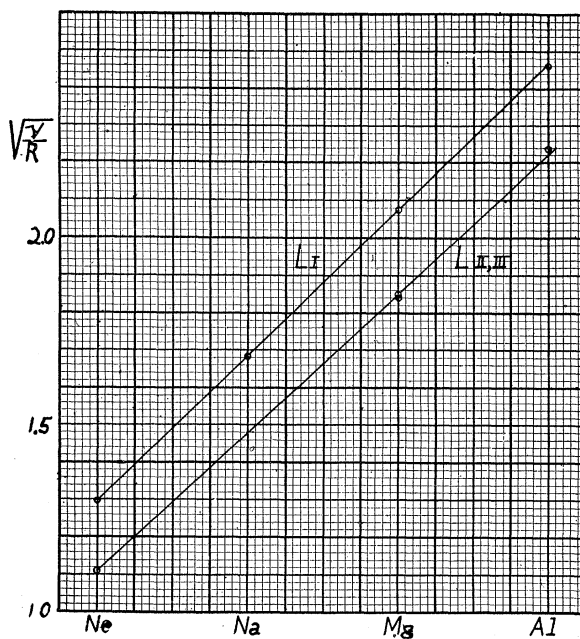


Fig. 1

but entirely without success. We have obtained with carbon electrodes a line at 585.7 Å where Lyman finds a significant helium line, but in view of the entire absence of the afore-mentioned series have attributed this

line to carbon alone. Since in these experiments we are exploding the tips of our electrodes with the use of enormously more concentrated energies than have ever been used in exploding wires this means that the helium spectra which have been reported from exploding wires are due to impurities. Ten years ago one of us obtained what were believed to be

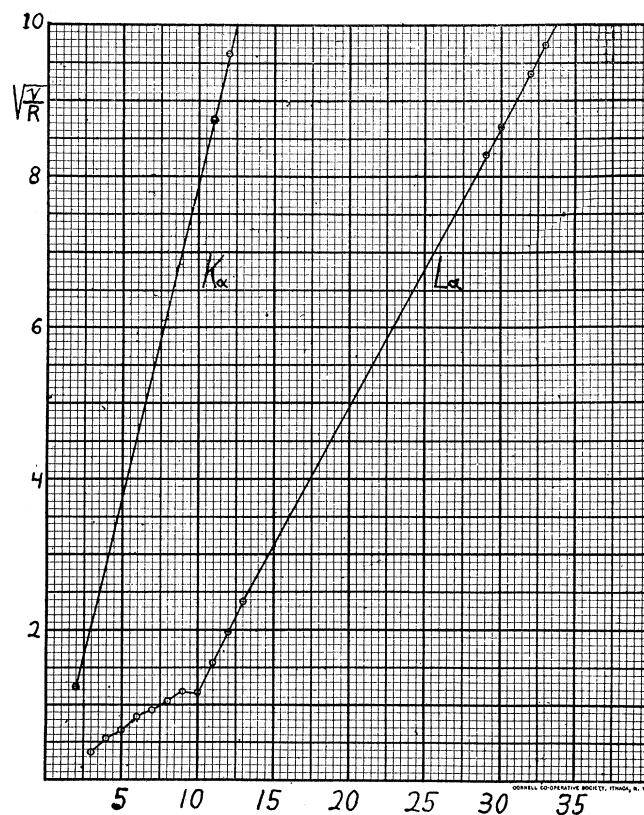


Fig. 2

helium lines in just this way from fresh electrode tips, but tired these lines out by repeated discharges, thus proving that they were due to impurities.

#### LITHIUM

The lithium spectrum was obtained from lithium metal held in pyrex tubes. As was to be expected the spectrum revealed the oxygen, hydrogen, and carbon lines. It showed also certain nitrogen lines of zero intensity and some weak silicon lines; but though the plate was an excellent one giving lines of the afore-mentioned elements from 370 Å up

to 1700 Å there were in this whole region no lithium lines whatever. This is striking proof that great gaps occur between the L and the K series in the optical region quite as well as in the x-ray field. The  $K\alpha$  line of lithium should occur at 240 Å which is within the region accessible to our measurements, but want of the best of gratings when we were working on lithium has prevented us from getting it thus far. If, following the convention used in the preliminary paper we designate by  $L\alpha$  the strongest line of the L spectrum (spectrum due to jumps to orbits of total quantum number 2) the  $L\alpha$  line of lithium should be the head of its doublet series, i.e. the ordinary red line of lithium. This is the line plotted in Fig. 2.

#### BERYLLIUM

The spectrum of beryllium was sought by using electrodes made by fusing a mixture of beryllium hydroxide  $\text{Be}(\text{OH})_2$  and borax  $\text{Na}_2\text{B}_4\text{O}_7$  into tubes of carbon and later of aluminum. After the characteristic lines of sodium, boron, oxygen, aluminum or carbon had been obtained no additional strong lines that could be certainly ascribed to beryllium were found, but there is one weak line of as yet uncertain identity which is listed in Table II. However, new experiments with metallic beryllium electrodes are now being undertaken and the results will be reported later. According to the results thus far found by other observers the beryllium spectrum begins on the short wave length side at 2175 Å and reaches its line of maximum strength at 3131.2 Å. This is the  $L\alpha$  line plotted in Fig. 2.

#### BORON

The spectrum of the atom of boron was obtained by inserting metallic boron bound together with fused borax in the cores of carbon tubes. Further, borax was used as a flux in the taking of spectra on eight other plates, each of which gave opportunity to see whether these same lines always appeared and whether they all failed to appear when borax was absent. The only lines of those given in Table III about the identification of which there has ever been the slightest uncertainty are the lines at 758.5 Å, 1230 Å, and 1362.7 Å. This last line had appeared in the spectrum obtained from the carbon electrodes and was at first thought to be due to carbon. But a comparison of all the plates taken when borax was used as a flux showed that it appeared in all of them, seven in number, in intensity from 3 to 8 while the most powerful carbon line at 1335.0 Å of intensity 15 did not appear at all in some of them and very weakly in others, unless carbon was used as electrode material. This meant that the line in question was surely due to boron. Its appearance in the spectrum

obtained from carbon electrodes meant either that boron was present as an impurity in the carbon or else that carbon had a line of its own so close to 1362.7 Å as to be indistinguishable from it with an instrument of the resolving power here used. To distinguish between these two alternatives we compare the boron and carbon spectra throughout and find that the strongest boron line, namely that at 1624.4 Å of intensity 8, just appears in intensity 1 in carbon, while this line at 1362.7 Å of intensity 5 in boron appears in intensity 5 in carbon, though the measured wavelength in carbon differs by the amount of .2 Å, which is too small a difference to be certainly resolvable. We conclude, therefore, that though boron is a very faint impurity in our carbon electrodes there is in all probability a carbon line as well as a boron line in the immediate neigh-

TABLE III

<i>Boron</i>					
Int.	$\lambda$	$\nu$		Int.	$\lambda$
5	676.8	147748		5	1362.7
0	731.2	136771		8	1624.4
3	758.5	131832	O <sub>2</sub>	0	1825.9
2	882.3	113336		0	1829.8
2	1081.7	92450		2	1842.9
1	1230.0	81301	C <sub>2</sub>		54262

borhood of 1362.7 Å and we record this line without comment under both boron and carbon. The foregoing is an illustration of the sort of analysis generally used in identifying lines. The final results for boron are found in Table III.

## CARBON

The carbon spectrum was obtained from electrodes made from gas carbon which showed as chief impurities, oxygen, nitrogen, silicon, hydrogen, and aluminum while traces of sodium, boron, and calcium also appeared. A comment upon the notation used in connection with the line at 538.4 Å and some other lines of less prominence may here be made. This line has been inserted under both carbon and oxygen but in each table the line is followed by the symbol of the other of these two elements with a subscript 2. This means, when the carbon table, for example, is under observation, that this line is in all probability carbon though it is a bare possibility that it is due to an oxygen impurity, while when the oxygen table is under inspection the line is in all probability due to oxygen though there is a bare possibility that it is here due to a carbon impurity. These two at first sight contradictory notations signify that we have very good evidence that both oxygen and carbon have a line at about this wave-length. If we felt altogether certain of this result we should omit in both tables the O<sub>2</sub> and the C<sub>2</sub> but we leave them in to in-

dicates the possibility of an error in this conclusion. The actual evidence in this case is as follows: Line 538.4 Å appears in intensity 7 with carbon electrodes when oxygen lines stronger than it do not appear there at all. This seems to show clearly that it is due to carbon. On the other hand it appears in intensity 4 with electrodes NaF—Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub>—Al when only the three strongest carbon lines appear and they with intensity zero.

TABLE IV

<i>Carbon</i>					
Int.	λ	ν	Int.	λ	ν
0	360.5	277408	0	960.6	104106
4	384.4	260166	0	966.6	103461
4	386.4	258826	12	977.1	102343
1	419.8	238197	10	1010.2	98990
1	450.9	221769	1	1022.8	97775
6	459.7	217552	11	1036.7	96461
1	493.7	202569	8	1066.0	93812
4	499.7	200140	3	1092.6	91522
1	511.7	195419	3	1137.4	87920
1	517.6	193192	4	1141.5	87608
2	530.3	188590	15	1175.6	85062
2	533.3	187501	3	1194.1	83743
7	538.4	185742	2	1230.2	81289
2	543.5	183993	7	1247.5	80158
2	549.6	181953	5	1262.4	79213
3	560.5	178399	5	1278.7	78204
3	564.7	177085	2	1296.8	77112
6	574.5	174052	1	1310.5	76307
3	585.7	170745	2	1322.3	75626
5	595.1	168045	7	1323.7	75544
1	600.2	166606	4	1329.4	75222
1	609.5	164061	15	1335.0	74909
1	617.7	161883	1	1356.2	73737
3	636.3	157149	5	1362.6	73391
5	641.8	155802	1	1426.9	70082
6	651.5	153483	1	1432.2	69822
0	661.5	151167	2	1463.7	68320
8	687.3	145491	1	1482.1	67473
0	711.0	140645	0	1527.9	65448
0	743.6	134486	0	1533.1	65226
0	749.6	133403	4	1548.8	64566
1	786.5	127141	3	1550.9	64481
5	799.9	125016	5	1561.3	64048
6	806.7	123957	0	1573.5	63552
5	810.0	123464	1	1577.6	63388
0	848.4	117876	0	1592.6	62792
5	858.5	116481	5	1657.6	60328
1	884.8	113026	2	1752.3	57068
10	904.1	110606	4	1760.7	56795
1	936.4	106798	1	1827.3	54727
4	945.6	105752	0	1832.8	54561
0	954.4	104775			

This means that this line in the spectrum must be ascribed to oxygen rather than to carbon since the study of the 28 other plates shows clearly that it cannot be due to sodium, fluorine, boron, or aluminum. These two lines of evidence taken together signify that in all probability there is a line in this region due to oxygen and another due to carbon.



The notation after the line at 600.2 Å in carbon means that this line is probably the same as the unquestioned oxygen line at 599.5 Å (see table 4) though the difference is a little more than the error of observation if both lines were sharply defined. The line at 600.2 Å in Table II, however, is weak and hard to measure accurately so that we wish to leave open the possibility that there may be a faint carbon line close to the strong oxygen line at 599.5 Å. The  $K_2$  after the  $O_1$  signifies that we wish to leave open the bare possibility that this line is due to potassium in which there is a strong line (see Table XV) of intensity 4 at 600.2 Å. Since potassium is a very oxidizable element this line too may be due to oxygen. It will be noticed that the line at 1194.1 Å is included in both the carbon and the silicon tables and that it is followed in the former by the symbol  $Si_1$  and in the latter by  $C_2$  thus indicating that it is probably due to silicon but possibly to carbon. The strong lines due to the 4 electron L-ring of carbon are all included between 360.5 Å and 1335.0 Å where the strongest carbon line is found (see Plate I). In harmony with the foregoing convention this is plotted in Fig. 2 as the  $L\alpha$  of carbon.

#### NITROGEN

The chief characteristics of the nitrogen spectrum were predicted before they were obtained experimentally. The carbon spectrum had been found beginning on the short wave-length side at about 360 Å, its lines gaining in intensity with increasing wave-length till they reached a powerful climax in the line at 1335 Å, which had been taken in accordance with the foregoing convention as the  $L\alpha$  line of carbon. Similarly the oxygen spectrum had been found beginning at about 140 Å and reaching an

TABLE V  
*Nitrogen*

Int.	$\lambda$	$\nu$	Int.	$\lambda$	$\nu$
0	660.3	151458	4	916.3	109132
1	671.5	148925	6	991.0	100912
5	685.5	145875	7	1085.2	92152
1	747.0	133871	2	1134.8	88124
3	764.1	130873	0	1190.6	83989
2	772.3	129480	0	1242.2	80500
2	775.9	128878	0	1492.9	66984

unmistakable maximum of intensity in the powerful line at 834 Å, the  $L\alpha$  line of oxygen. A general progression of spectra with atomic number toward higher and higher frequencies had been unmistakably observed, but no nitrogen lines in the extreme ultra-violet were known at all except the 1492.8 and 1494.8 lines reported by Lyman. It was clear from this progression that a strong  $L\alpha$  nitrogen line must exist between 834 Å and 1335 Å since the atomic number of nitrogen lay between that of carbon

and oxygen. Accordingly ammonium nitrate was fused into the cores of aluminum electrodes and the spectrum shown in Table V was at once obtained with its strong line at 1085.2 Å (see Plate I). This spectrum was also checked by using sodium nitrite in carbon electrodes.

#### OXYGEN

The oxygen spectrum is given in Table VI. The method of obtaining it has been already detailed. It will be noticed that all of the lines save one of wave-length above the very strong line at 834 Å have a zero intensity while that one has an intensity of but 1. This is strikingly shown in

TABLE VI

#### Oxygen

Int.	$\lambda$	$\nu$		Int.	$\lambda$	$\nu$	
0	136.6	732332	Al	0	562.0	177949	
0	144.3	692809	Al	0	567.5	176199	Al
0	219.1	456413?	Al	0	580.6	172230	
0	221.5	451508?	Al	1	597.7	167314	
0	225.9	442693?	Al	5	599.5	166800	
0	233.8	427807		2	608.3	164398	
1	238.6	419041		3	610.1	163913	
0	260.7	383583		3	616.7	162161	
0	267.1	374420		4	625.2	159946	
0	272.4	367121		3	629.6	158823	
1D	279.7	357513		3	644.0	155272	
1	295.8	338043		0	656.7	152270	Al <sub>2</sub>
2	303.7	329294		0	658.4	151879	Al <sub>2</sub>
3	305.7	327129		0	673.0	148586	
1	321.5	311003		6	703.1	142225	
1	328.7	304210		5	718.5	139187	
0	345.7	289302		2	760.3	131536	
0	352.9	283366	Mg	0	764.7	130763	N <sub>1</sub>
0	355.3	281444	Mg	0	774.3	129151	
0	359.4	278211		2	779.8	128246	
4	374.3	267180		3	787.4	126997	
0	379.6	263435		3	790.1	126561	
2	395.7	252691		1	796.4	125562	
1	430.0	232585		0	802.0	124694	Al <sub>3</sub>
2	434.5	230129		8	834.0	119904	
0	481.1	207853		0	898.8	111264	
2	484.7	206322		0	921.1	108568	
5	507.8	196943		1	923.1	108328	
0	515.5	194005		0	1025.6	97507	H
0	518.2	192965	C <sub>2</sub>	0	1031.4	96952	
4	525.7	190223		0D	1152.6	86760	
2	538.4	185729	C <sub>2</sub>	0	1195.5	83646	Mg <sub>3</sub>
0	540.7	184939		0	1338.5	74711	
5	554.2	180453		0	1343.5	74435	Al <sub>2</sub>

Plate I. The oxygen spectrum shown on this plate does not, however, extend below about 500 Å but in the so called aluminum spectrum shown in Plate II all of the strong lines below 400 Å are due to oxygen.

#### FLUORINE

The fluorine spectrum was obtained through the use of sodium fluoride in the cores of aluminum electrodes. It contains but two strong lines at

607 Å and at 656.4 Å, the latter of which is taken, according to the foregoing convention, as the  $L\alpha$  line of fluorine. This line unfortunately does

TABLE VII

*Fluorine*

Int.	$\lambda$	$\nu$		Int.	$\lambda$	$\nu$	
0	378.6	264152	?	1	571.4	175009	
0	411.3	243149		7	606.9	164772	
1	420.1	238027		5	656.4	152351	
0	441.7	226408		0	694.0	144092	
0	445.3	224548		0	954.9	104728	C
0D	458.0	218355	Si	0	984.4	101586	Cl <sub>3</sub>
1	464.9	215109		0	989.3	101077	
0	472.2	211779		0	1049.6	95271	
1	490.3	203944		0	1133.5	88219	
0	497.6	200973		0	1143.7	87439	
0	547.2	182745		0	1151.8	86822	0
2	567.5	176224	O <sub>2</sub> , Al <sub>3</sub>				

not show distinctly in the reproduction in Plate I. Indeed each of the accompanying reproductions fails to reveal some lines which are distinct on the original negatives.

## SODIUM

The sodium spectrum obtained from electrodes of pure sodium as well as from sodium fluoride in aluminum tubes shows in both plates only one unmistakable line in the whole region studied (300 Å to 2000 Å) namely that at 372.3 Å. The line at 376.6 Å also appears definitely on the plate taken with pure sodium electrodes as can be seen clearly from Plate II, though it does not appear on the plate taken with sodium fluoride electrodes. Deficiency of intensity may perhaps be the cause of its absence in this latter case. There can scarcely be any trace of a doubt that the line at 372.3 Å is the line of greatest intensity in the L spectrum of sodium, for a line is definitely predicted by the Bohr theory at this wave-length.

TABLE VIII

*Sodium*

Int.	$\lambda$	$\nu$	Int.	$\lambda$	$\nu$
2	372.3	268637	1	376.6	265562

This prediction is obtained as follows: The single electron in the outmost or M shell of the normal sodium atom is in an energy level whose frequency value is represented by the convergence frequency of the principal series of sodium  $\nu_M = 41449.0$  ( $\lambda = 2412.63$ ). When an electron is removed from the L shell of sodium the foregoing M electron jumps into its place. The frequency value  $\nu_L$  of the level to which it jumps is related to the frequency  $\nu_e$  of the emitted line and  $\nu_M$  by the Kossel equation

$$\nu_e = \nu_L - \nu_M \quad (1)$$

$\lambda$  372.3 Å corresponds to  $\nu_e = 268640$ . These values of  $\nu_M$  and  $\nu_e$  give  $\nu_L = 310,090$ , whence  $\nu_L/R = 2.8258$ , and  $\sqrt{\nu_L}/R = 1.6810$ . Now the

values of  $\sqrt{\nu_L/R}$  for the  $L_{II}$   $L_{III}$  levels of aluminum, magnesium, sodium, and neon are as follows: Al=2.28<sup>2</sup>; Mg=1.87<sup>2</sup>; Na=1.49<sup>3</sup>; Ne=1.11.<sup>4</sup>

The observed line at 372.3 Å cannot then correspond to the jump to  $L_{II}$  or  $L_{III}$  and must therefore correspond to the jump to the only remaining L level, namely  $L_I$  and we are now for the first time enabled to fix the value of the  $L_I$  energy level<sup>2</sup> in sodium at the above value,  $\nu/R=2.8258$ . That this is correct will be shown in the next section by comparing it with the  $L_I$  levels for both neon and magnesium.

#### MAGNESIUM

Table IX shows that there are but three reasonably strong magnesium lines in the whole range of our plates (see Plate II) and the position of these lines at 231.6 Å, 320.9 Å, and 323.2 Å shows that they must belong to the L spectrum of magnesium. The very weak lines at 353 Å and 355 Å are probably due to oxygen. The other four weak magnesium lines which are in the neighborhood of 1700 Å belong, the first two to the second term of the diffuse series of ionized magnesium and the last two to the second term of the sharp series.<sup>5</sup>

The Bohr theory predicts all of our three observed magnesium lines in the L series as follows.

TABLE IX

<i>Magnesium</i>			
Int.	$\lambda$	$\nu$	
2	231.6	431760	
5	320.9	311643	
4	323.2	309377	
0	352.9	283366	O
0	355.3	281444	O

Int.	$\lambda$	$\nu$	
0	1735.2	57630	<i>II</i> ,* $3p_2-4d^\dagger$
1	1737.9	57540	<i>II</i> , $3p_1-4d$
0	1751.0	57110	<i>II</i> , $3p_2-5s$
0	1753.7	57021	<i>II</i> , $3p_1-5s$

\* II means the singly ionized atom, i.e., the atom with one electron entirely removed.

III means the doubly ionized atom, i.e., two electrons entirely removed.

† The series notation used is that introduced by Bohr (Ann. d. Physik **71**, p. 286) and now adopted by Fowler and Paschen.

There are two electrons in the M shell of magnesium both in orbits of the form  $3_1$  (total quantum number 3, azimuthal quantum number 1).<sup>2</sup> The only possible jumps from these orbits are into the  $L_I$   $L_{II}$   $L_{III}$  orbits. The last two jumps should correspond to a doublet, the  $l\eta$  doublet of Bohr's most recent notation, the jump to  $L_I$  should correspond to his single line  $\beta_4$ . Consider first the jumps into the  $L_{II}$   $L_{III}$  orbits. These are from the  $M_I$  orbit according to Bohr and Coster. The frequency

<sup>2</sup> Bohr and Coster, Zeits. f. Phys. **12**, 344-352, 1923

<sup>3</sup> This value is interpolated from the two adjoining ones.

<sup>4</sup> Computed from Horton and Davies ionization potential 16.7 volts, Roy. Soc. Proc. **98**, 124-146, 1920

<sup>5</sup> Fowler, Series in Line Spectra

value of the 3(1,1) level is the convergence frequency of the principal series of magnesium singlets<sup>6</sup> for which  $\nu = 61672.1$ .<sup>5</sup> Applying then Eq. (1) to each of our observed lines  $\lambda$  320.9 Å ( $\nu = 311640$ ) and  $\lambda$  323.2 Å ( $\nu = 309380$ ) we obtain  $\nu_{LII} = 373,310$ ;  $\nu_{LIII} = 371,050$ ; whence  $\nu_{LII}/R = 3.4019$ , and  $\nu_{LIII}/R = 3.3813$ ,  $\sqrt{\nu_{LII}}/R = 1.8444$ ,  $\sqrt{\nu_{LIII}}/R = 1.8388$ .

Heretofore these levels have been obtained by computation from the K absorption edge and the K $\alpha$  lines, and the experimental data have not been sufficiently exact to differentiate between these two near-by levels. Bohr and Coster give the average level as 3.5 and Sommerfeld as 3.46. Our L<sub>II</sub> L<sub>III</sub> levels, which should be correct to about 0.1 percent, are in quite as good agreement with the approximate values given by Bohr and Coster and by Sommerfeld as could be expected from the sort of precision obtainable from the use of the K series data.

Again, according to Sommerfeld's analysis, the frequency difference between the L<sub>II</sub> L<sub>III</sub> levels is given by the equation<sup>7</sup>

$$\Delta\nu_L = \Delta\nu_H(Z-s)^4 \quad (2)$$

in which  $\Delta\nu_H$  is the frequency separation of the hydrogen doublet the value of which is .365 cm<sup>-1</sup>, and  $(Z-s)$  is the effective nuclear charge. For the atoms of high atomic number  $Z$ , the value of  $s$  is 3.5. Inserting our observed separation  $\Delta\nu_L = 2260$ , and the value of  $Z$ , namely 12, and solving for  $s$ , the result is  $s = 3.1$ . This is fairly close to the observed "screening constant" for large  $Z$ 's. But according to the Bohr theory of the interpenetration of the electrons from the M, N, etc., shells, the value of  $s$  should be somewhat less for atoms devoid of shells beyond the L shell. In other words for atoms near neon  $s$  may be expected to be somewhat smaller than 3.5 as it is here found to be. Indeed from the L doublet in neon as given by Grotian<sup>8</sup> and Eq. (2) the value of  $s$  for neon is found to be 3.2 or within the limits of our error exactly the same as we find it to be for magnesium. This is very beautiful proof that our observed magnesium lines at 320.9 Å and 323.2 Å are in fact the L doublet of magnesium (see Plate II).

Returning now to the very sharply defined singlet at 231.6 Å. If Bohr's general scheme<sup>5</sup> were of universal applicability this would correspond to the  $\beta_4$  line as already indicated, but Bohr himself shows that the 3(2,1) or M<sub>II</sub> level does not exist, and that this sort of lack is common to all the substances having the alkali-earth type of spectrum.<sup>6</sup> The only M levels, not barred out here by the selection principle, which are actually revealed by the optical series in magnesium are those of fre-

<sup>6</sup> Bohr, Ann. der Phys. **71**, 281-288, 1923

<sup>7</sup> Sommerfeld, Atombau and Spectrallinien, pp. 607-618

<sup>8</sup> Grotian, Zeits. f. Phys. **8**, 116, 1921

quency value  $\nu=39801$  and  $\nu=26620.7$ . If in the normal atom of magnesium one of the two electrons were in one of these two levels, the first one, that corresponding to the smallest potential energy, would naturally be its most probable location. The actual jump of this electron would then be from this  $M_{III}$  or  $3(2,2)$  level to the  $L_I$  or the  $2(1,1)$  level. Even if, in the normal magnesium atom, no electron is in a  $3_2$  level (Bohr places the two outer magnesium electrons in  $3_1$  orbits) yet an electron, once removed from the  $L_I$  level, would have to return to it through a  $3_2$  level, and in accordance with all spectroscopic behavior the most likely line to be excited would be that corresponding to the smallest permitted energy change. This would be the change to  $L_I$  from  $\nu=39801$ . We can, then, locate with the aid of Eq. (1) this  $L_I$  level from our observed line at  $\lambda\ 231.6$  ( $\nu=431,800$ ) and the  $M$  level at  $\nu=39801$ .

Thus  $\nu_{LI}=471,600$  and  $\nu_{LI}/R=4.298$ ;  $\sqrt{\nu_{LI}}/R=2.073$ .

When the position of this  $L_I$  level for magnesium is compared with the position of the same  $L_I$  level just found for sodium and with that computed from the Horton and Davies value of the third or highest ionization potential of neon, namely 22.8 volts, which gives  $\nu_{LI}=184,680$ ,  $\nu_{LI}/R=1.683$ ,  $\sqrt{\nu_{LI}}/R=1.297$ , the straight line relation shown in Fig. 1 is obtained. This may be taken as an excellent indication that these three  $L_I$  levels are correctly located and also as justification of the foregoing statement that all three observed  $L$  lines of magnesium are accurately predicted by the Bohr theory.

#### ALUMINUM

Plate II and the spectrum labelled O in Plate I show the lines obtained with "chemically pure" aluminum electrodes. In these photographs the strong carbon, silicon, and hydrogen lines appear faintly and the oxygen lines, identical with those found with magnesium, very powerfully. Plate III however brings out the characteristic Al lines much better, though boron and fluorine lines are also present here. All of the lines in any of these plates which either are or may be due to aluminum are given in Table X. It is noteworthy that of the very few aluminum lines below 1000 Å, the two at 695.9 Å and 856.8 Å have very recently been predicted precisely as here found, by Paschen<sup>9</sup> through the working out of the spectrum due to the aluminum atom when stripped of all of its valence electrons, Al(III). It is remarkable also that all of our strongest aluminum lines like those at 1353.0 Å, 1379.7 Å, 1384.5 Å, 1605.9 Å, 1612.0 Å, 1854.7 Å, and 1862.7 Å belong to Al(III), which seems to show that the aluminum atoms exist most abundantly in our sparks

<sup>9</sup> Paschen, *Ann. der Phys.* **71**, 152, 1923

in this entirely stripped state. The only good plate which goes down to 136 Å shows two scarcely mistakable lines at 136.6 Å and 144.3 Å which were originally thought to be the strongest lines of the L spectrum of aluminum and were so reported in a preliminary communication, but for theoretical reasons to be presently detailed, we have been obliged to conclude that these two lines are due to oxygen. Between the lines at 144.3 Å and 230.8 Å there are found a number of very faint lines about the reality of some of which there was some uncertainty. Each of us measured these lines independently before we had made any theoretical calculations whatever and retained only those upon which we agreed. We then found that four of the seven lines thus obtained gave very strong theoretical evidence that they belonged to the spectrum of aluminum. This evidence is as follows.

TABLE X  
*Aluminum*

Int.	$\lambda$	$\nu$		Int.	$\lambda$	$\nu$	
0	136.6	732332	O	4	1379.7	72478	III, $3p_2-4s$
0	144.3	692809	O	4	1384.5	72229	III, $3p_1-4s$
0	162.4	615839	?	0	1540.3	64921	
0	186.9	534988	?	5	1605.9	62272	III, $3p_2-3d$
0	200.0	499950	?	5	1612.0	62036	III, $3p_1-3d$
0	219.1	456413	? O	4	1671.0	59844	
0	221.5	451508	? O	3	1721.0	58105	II, $3p_2-3d$
0	225.9	442693	? O	2	1725.6	57950	II, $3p_1-3d$
0	230.8	433332	?	0	1750.4	57129	
0	656.7	152270	O <sub>I</sub>	2	1760.7	56797	II
0	658.4	151879	O <sub>I</sub>	2	1764.4	56676	II
1	695.9	143707	III, $3s-4p$	2	1768.4	56549	II
0	802.0	124694	O <sub>I</sub>	0	1774.2	56365	
0	856.9	116707	III, $3p_1-5s$	0	1777.5	56258	
0	1264.8	79066	Si <sub>I</sub>	0	1818.8	54980	
1	1343.5	74435	O	10	1854.7	53917	III, $3s-3p_1$
1	1353.0	73909	III, $3d-5f$	10	1862.7	53685	III, $3s-3p_2$

In the normal atom of aluminum the 3 outer or M electrons are according to Bohr<sup>10</sup> in the  $3_1$  and  $3_2$  levels. When, then, an L electron is knocked out it is to be expected that it will be most frequently replaced by a jump from a  $3_1$  or a  $3_2$  level. But in normal aluminum no  $3_1$  level has been observed spectroscopically,<sup>6</sup> so that the jump to be expected most frequently is that from the observed  $3_2$  level having a frequency value of 48168<sup>5</sup> to the L<sub>I</sub> or the L<sub>II</sub> L<sub>III</sub> levels. Assuming that both of these jumps occur we can find at once from the Kossel relation the frequency values of these two levels (the L<sub>II</sub> L<sub>III</sub> levels are so close together at this value of atomic number that our plates would not resolve them) as soon as we have an observed line corresponding to these jumps. Computing in this way, with the use of the lines at 162.4 Å and 200.0 Å, we ob-

<sup>10</sup> Bohr, Ann. der Phys. **71**, 260, 1923

tain  $\nu_{\text{LI}} = \nu_{162.4} + \nu_{\text{MIII}}; \nu_{\text{LI}} = 615,800 + 48,168 = 664,000$ . Similarly  $\nu_{\text{LII LIII}} = \nu_{200.0} + \nu_{\text{MIII}}; \nu_{\text{LII LIII}} = 500,000 + 48,168 = 548,200$ .

But if the foregoing assumptions are correct it should be possible to find other jumps to these same levels. Thus we already know that Al(III) exists in our source and Paschen has recently worked out fully its spectral series and located its  $3_1 3_2 3_3$  levels at frequencies of 229,450, 175,690, and 113,500. By analogy with sodium, in which we found the jump from the  $3_1$  level to the  $L_I$  level the only one which appeared on our plates, it will here be assumed that the most likely jump in Al(III) will be to  $L_I$  from  $\nu = 229,450$ . Combining this frequency with that of the observed line at 230.8 Å we have  $\nu_{\text{LI}} = \nu_{230.8} + \nu_{\text{MII}}; \nu_{\text{LI}} = 433,300 + 229,450 = 662,800$ , which agrees within one part in 600 (better than our observational error) with the  $L_I$  level as located from the use of line 162.4 Å.

Again there is another observed level in the Al(I) spectrum, namely that at 15,845,<sup>5,6</sup> which corresponds to the  $3_3$  orbit. The only jump permitted by the selection principle from this level is to the  $L_{\text{III}}$  level.<sup>2</sup> Assuming that this jump gives rise to our line at 186.9 Å we have  $\nu_{\text{LIII}} = \nu_{186.9} + \nu_{\text{MV}}; \nu_{\text{LIII}} = 535,000 + 15,845 = 550,800$ .

The agreement between this result and the foregoing computation of the  $L_{\text{III}}$  level from the use of line 200.0 Å is not quite as good as in the case of the  $L_I$  level, but an error of .4 Å in our measurement of each of the lines would account for the difference. With very faint lines such as these are such an error is admissible, though scarcely with the stronger and sharper lines. Taking the means of each set of determinations of levels we have then the following final values for aluminum:

$$\nu_{\text{LI}} = 663,400; \nu_{\text{LII LIII}} = 549,500.$$

We can now obtain an entirely independent check upon these levels as follows. We have:  $\nu_{\text{LI}}/R = 6.045$ ;  $\nu_{\text{LII LIII}} = 5.008$ ;  $\sqrt{\nu_{\text{LI}}/R} = 2.459$ ;  $\sqrt{\nu_{\text{LII LIII}}/R} = 2.238$ . Fig. 1 shows that the value of the  $L_I$  level thus obtained is exactly where an extrapolation from the corresponding levels found above for neon, sodium, magnesium would place it. The evidence then that we have now correctly located this level is quite satisfactory. Our  $L_{\text{II}} L_{\text{III}}$  level for aluminum will be seen from the lower line of the figure to be a trifle higher than an extrapolation from the corresponding levels in neon and magnesium would place it. This raises some question as to the correctness of our determination of the  $L_{\text{II}} L_{\text{III}}$  level in aluminum. The four lines at 230.8 Å, 200.0 Å, 186.9 Å, and 162.4 Å are the only ones of the seven observed lines in this region which seem to be obtainable from any possible jumps in the aluminum atom, although the Al(II) levels very recently worked out by Paschen<sup>11</sup> have been tried. If the  $L_I$

<sup>11</sup> Paschen, Ann. der Phys. **71**, 537, 1923



level has been correctly obtained in the foregoing, then it is improbable that any lines exist in the L spectrum of aluminum of higher frequency than the frequency value of the  $L_I$  level, namely  $\nu=663400$  or  $\lambda$  151 Å. Since the lines at 136.6 Å and 144.3 Å are both of higher frequency or shorter wave-length than these values, they cannot be due to the knocking of a single electron from the L ring of aluminum. As indicated above, therefore, we think it probable that these two lines are due to oxygen, which is furnishing practically all the strong lines below 1000 Å, though they may possibly be due to the removal of two electrons from the L shell of the aluminum atom.

## SILICON

Table XI and Plate III show the lines due to silicon. These were obtained both from the use of the element as electrodes and from that of sodium silicate. The twelve lines indicated by "IV" all belong to the

TABLE XI

*Silicon*

Int.	$\lambda$	$\nu$		Int.	$\lambda$	$\nu$	
1	361.6	276549	IV, $3s-5p$	0	1194.4	83731	C <sub>2</sub>
1	392.7	254647		5	1206.5	82884	
3	457.7	218503	IV, $3s-4p$	0	1228.1	81425	IV, $4p_1-6s$
0	486.6	205516		0	1250.3	79981	
2	815.0	122704	IV, $3p_2-4s$	1	1260.5	79337	
2	818.0	122257	IV, $3p_1-4s$	1	1264.9	79056	Al
0	994.6	100540		1	1294.9	77228	
0	997.5	100251		2	1299.0	76981	
0	1066.7	93746	IV, $3d-4f$	1	1303.5	76717	
0	1086.9	92005	?	0	1309.5	76368	?
2	1108.9	90177		6	1393.9	71742	IV, $3s-3p_1$
2	1110.3	90064		6	1403.0	71276	IV, $3s-3p_2$
2	1113.5	89807		0	1416.8	70583	
2	1122.6	89083	IV, $3p_2-3d$	0	1500.9	66625	
2	1128.4	88623	IV, $3p_1-3d$	0	1526.9	65493	?C
1	1143.3	87466		0	1533.4	65213	IV, $4d-6f$
1	1164.0	85908	?				

spectrum of the silicon atom completely stripped of its valence electrons Si(IV) as very recently worked out by Fowler.<sup>12</sup> It is to be noted that all the strongest lines belong to this completely stripped silicon atom thus indicating that, as in the case of aluminum, this type of ionization is extremely common in our vacuum sparks.

## PHOSPHORUS

The phosphorus lines were obtained from aluminum electrodes having phosphorus in their cores and also from a flux of borax and sodium phos-

<sup>12</sup> Fowler, Roy. Soc. Proc. **103**, 423, 1923

phate fused into aluminum electrodes. Table XII and Plates III and IV show the spectra thus obtained.

The tables already published by Paschen<sup>9</sup> and by Fowler<sup>12</sup> giving the experimental progression of the series terms for Na(I), Mg(II), Al(III), Si(IV) should make it possible to extrapolate from this progression to P(V) and thus to find lines to be expected from phosphorus when stripped of all of its valence electrons. Thus the level corresponding to the convergence frequency of the fundamental series ( $3_3$ ) is  $12,800 \times 25 = 320,000$ , that of the diffuse series ( $3_2$ ) is  $17,450 \times 25 = 436,250$ , and that of the principal series ( $3_1$ )  $21,200 \times 25 = 530,000$ . From these extrapolations the first term of the principal series ( $3s-3p$ ) is  $\nu = 93,700$ , and that of the

TABLE XII

*Phosphorus*

Int.	$\lambda$	$\nu$		Int.	$\lambda$	$\nu$	
3	824.5	121292		1	997.9	100211	
3	827.9	120789		1	999.4	100062	
1	847.6	117984		1	1002.8	99721	
3	855.5	116891		1	1015.3	98491	
4	859.6	116335		1	1025.3	97530	H
0	865.5	115541		0	1027.9	97282	
2	871.3	114771	$V, 3p_2-3d$	3	1030.3	97056	
2	877.4	113968	$V, 3p_1-3d$	1	1032.9	96817	
1	908.2	110112		1	1035.3	96589	
1	913.8	109431		5	1117.9	89457	$V, 3s-3p_1$
2	916.8	109077		3	1127.8	88670	$V, 3s-3p_2$
2	918.4	108891		0	1153.6	86687	
1	921.7	108494		1	1198.7	83423	O
6	950.6	105202		0	1287.9	77649	
3	964.5	103676		0	1646.5	60737	

diffuse series ( $3p-3d$ ) is  $\nu = 116,250$ . Similarly the progression of the doublet separation for Na(I), Mg(II), Al(III), and Si(IV) as given by Fowler makes it possible to obtain by extrapolation the doublet separation for P(V) which thus is found to be about  $800 \text{ cm}^{-1}$ . Two of the strongest doublets in our phosphorus spectrum, namely those at  $\lambda\lambda$  871.3, 877.4;  $\nu = 144,771$ , 113,968, and  $\lambda\lambda$  1117.9, 1127.8;  $\nu = 89457$ , 88670 have the correct separation and are in the correct position within the limits of uncertainty of our extrapolation. It is hoped that further series relationships can soon be worked out.

## SULPHUR

The sulphur spectrum was obtained from the element in aluminum tubes and also from sodium sulphate in such tubes. It will be seen to be characterized by a very large number of lines (see Table XIII and Plates III and IV) as is to be expected from the large number of its valence electrons combined with the foregoing evidence that from one to all of

these may be stripped off in our vacuum sparks, each of course thus adding a new set of series. Series relationships ought to be obtainable from the pursuit of the method indicated under phosphorous but the search obviously becomes more and more difficult with increasing complexity of spectra.

TABLE XIII

<i>Sulphur</i>					
Int.	$\lambda$	$\nu$	Int.	$\lambda$	$\nu$
0	370.2	270124	1	758.5	131843
0	439.1	227744	5	764.7	130779
0	465.2	214943	4	774.2	129164
0	476.5	209864	5D	786.6	127133
1	485.0	206194	2	790.0	126587
1	500.4	199856	4	796.9	125483
1	521.1	191909	3	800.1	124981
0	539.6	185340	3	804.3	124327
2	551.0	181485	5	809.2	123585
2	554.0	180512	3	816.0	122546
0	560.3	178845	2	824.5	121292
0	564.3	177208	2	827.0	120915
0	568.3	175957	2	837.0	119474
0	572.0	174831	2	841.1	118895
0	577.7	173115	2	844.0	118478
0	585.2	170885	1	849.2	117754
0	594.1	168325	2	852.6	117283
0	607.9	164498	2	854.8	116988
3	611.4	163564	1	857.6	116604
0	628.0	159243	1	860.6	116205
1	641.3	155941	2	866.9	115356
1	646.7	154631	0	890.8	112260
4	652.9	153172	2	894.9	111751
4	654.6	152772	2	907.0	110251
4	656.6	152295	2	911.4	109720
3	658.5	151863	2	915.3	109256
5	661.4	151188	2	919.3	108784
3	665.3	150310	1	924.2	108198
1	669.7	149330	1	933.7	107105
3	675.0	148159	3	937.7	106642
4	677.4	147628	1	945.0	105826
5	679.9	147083	0	971.0	102983
4	682.1	146608	1	978.2	102231
1	692.0	144502	0	981.9	101846
2	696.2	143635	1	996.3	100373
4	699.2	143019	5	1014.8	98544
4	701.4	142576	5	1021.3	97919
4	703.7	142110	2	1031.5	96951
3	707.9	141271	0	1050.3	95213
4	711.0	140639	3	1063.0	94075
4	716.9	139484	3	1073.4	93161
4	722.0	138498	2	1077.6	92798
4	725.2	137887	0	1190.5	84002
5	729.4	137097	1	1194.0	83752
2	735.1	136038	4	1200.8	83275
3	741.6	134845	1	1204.6	83015
5	745.2	134192	0	1250.2	79990
5	749.5	133424	1	1253.7	79763
3	753.8	132668	3	1259.3	79409

## CHLORINE

The chlorine spectrum was taken with sodium chloride and borax in aluminum electrodes. Sodium, aluminum, and boron have practically

no lines in the region studied, while the oxygen lines are well known. The chlorine spectrum has, like the sulphur, a multitude of strong lines. Results are shown in Table XIV and Plates III and IV.

TABLE XIV

*Chlorine*

Int.	$\lambda$	$\nu$		Int.	$\lambda$	$\nu$	
1	528.3	189294		6	960.4	104121	
4D	536.7	186327		2	973.0	102771	
0	542.5	184318	? C	4	977.2	102335	C
2	549.7	181907		4	984.8	101546	
3	553.1	180789	? O	3	1005.4	99461	
4	556.4	179714		4	1008.6	99145	
4	561.5	178094		4	1014.9	98535	
3	565.1	176966		3	1063.6	94019	
3D	569.7	175537		3	1068.2	93615	
4D	574.3	174122		4	1070.9	93381	
3	584.6	171057		3	1079.0	92683	
4	586.9	170384		0	1128.0	88655	
3	591.5	169071		2	1145.0	87336	
3	595.8	167833		0	1200.5	83296	
3	606.3	164938	F	2	1302.0	76807	
3	609.3	164112		2	1305.1	76623	
2	612.2	163353		2	1331.2	75120	
2	618.2	161755		1	1344.0	74405	
2	621.1	161018		3	1347.2	74230	
2	623.7	160341		2	1351.6	73984	
4D	635.8	157272		2	1354.6	73824	
3	639.1	156460		0	1418.4	70504	
4	653.7	152980		0	1428.3	70013	
4D	663.2	150780		1	1462.3	68386	
3	670.8	149080		1	1465.8	68222	
3	682.2	146585		1	1542.1	64849	
1	689.6	145022		0	1548.2	64591	C
4	707.4	141363		0	1551.2	64466	C
4	712.6	140323		0	1561.0	64061	C
4	715.8	139706		0	1565.1	63893	
5	718.7	139144	O <sub>2</sub>	2	1577.7	63383	
2	725.4	137849		0	1590.7	62866	
3	729.4	137105		0	1593.5	62756	
2	777.5	128622		0	1656.8	60359	?
4	787.8	126936		1	1663.1	60129	?
3	793.3	126053		0	1808.0	55309	?
6D	840.9	118926		0	1812.4	55175	?
4	851.6	117426		1	1817.8	55012	
4	864.4	115690		2	1821.9	54888	
4	888.0	112618		2	1832.1	54584	
4D	893.5	111918					

## POTASSIUM

The potassium spectrum was obtained from the use of potassium acid borate in aluminum tubes. In the region of wave-length which we are investigating there are of course no potassium lines due to the single electron in its N shell. Yet Table XV and Plate IV reveal a very considerable number of rather faint lines extending from 312 Å up to 1303 Å. These lines must then be due to the removal of some of the 8 electrons of the M shell, i.e. they may be definitely classified as belonging to the M

spectrum of potassium. In view of the complexity of this spectrum we have been unable to find any confirmations of the Bohr theory such as we found in the case of sodium.

TABLE XV  
*Potassium*

Int.	$\lambda$	$\nu$		Int.	$\lambda$	$\nu$	
0	312.9	319632		0	474.9	210557	
0	341.7	292654		0	479.1	208720	
0	344.9	289922	O	1	495.1	201967	
0	355.1	281643	O <sub>2</sub>	1	520.3	192182	
0	362.7	275748	?	2	580.6	172233	O <sub>2</sub>
1	379.9	263227		4	600.2	166617	O <sub>1</sub>
2	382.5	261411		3	612.5	163279	
2	390.1	256318		4	644.8	155096	O <sub>1</sub>
2	392.7	254654		0	724.4	138045	
0	399.3	250432		1	737.0	135691	
0	402.3	248546		1	742.1	134745	
2	409.8	243998		2	745.3	134174	
2	414.4	241324		1	750.0	133326	
1	418.0	239263		1	754.6	132522	
0	422.1	236888		3	765.7	130608	
0	425.6	234984		3	778.6	128442	O <sub>1</sub>
0	441.6	226449		3	796.8	125500	O <sub>1</sub>
2	444.4	225043		0	873.1	114541	
2	448.5	222985		1	878.7	113801	
0	466.5	214358		1	1303.6	76711	
4	470.4	212571					

#### CALCIUM

The spectrum of calcium was obtained with calcium electrodes and consists, as Plate IV and Table XVI show, of a very few strong lines upon a background of a considerable number of faint ones, so faint that they scarcely show upon the plate. It is possible to fit some of these strong lines into the Bohr theory precisely in the manner used in analyzing the spectrum of magnesium. Thus the separation of the M<sub>II</sub> M<sub>III</sub><sup>13</sup> doublet is computable as in case of the L<sub>II</sub> L<sub>III</sub> doublet discussed above. Thus:<sup>7</sup>

$$\Delta\nu_m = \Delta\nu_m(Z-s)^4$$

in which  $\Delta\nu_H$ , since it now corresponds to the M series instead of the L, has the value  $(8/27) \times .365^{-1}$  cm. =  $.108^{-1}$  cm. Inserting the separation of the strong doublet  $\lambda = 655.9 \text{ \AA}, 669.6 \text{ \AA}, \nu = 152460, 149350$  and therefore  $\Delta\nu_m = 3110$ , and then solving for the screening constants, there results  $s = 7$ . The value of  $s$  given by Sommerfeld<sup>7</sup> for the M<sub>II</sub> M<sub>III</sub> doublet is  $s = 8.3$ . Our value is somewhat less than this as it should be because of the fact that the M shell is here not entirely full. The result is therefore close enough to the value to be expected to furnish quite satisfactory evidence that the chosen doublet is in fact the M<sub>II</sub> M<sub>III</sub> doublet of calcium.

<sup>13</sup> For notation see Bohr and Coster<sup>2</sup>

The frequency value of the  $M_{II}$   $M_{III}$  levels can now be computed precisely as in the case of the L series of magnesium. We there found that the jump from the  $M_I$  level to the  $L_{II}$   $L_{III}$  levels corresponded to our observed magnesium L doublet. Similarly the jump from the  $N_I$  level to the  $M_{II}$   $M_{III}$  levels may be expected to correspond to the M doublet. The frequency value of the  $N_I$  level, which is the convergence frequency of the principal series of calcium singlets has the value  $\nu=49,305^5$ . We have then the equation  $\nu_{MII}=\nu_{655.9}+49,305$ ;  $\nu_{MII}=152,460+49,305=201,770$ , and similarly  $\nu_{MIII}=\nu_{669.6}+49,305$ ;  $\nu_{MIII}=149,350+49,305=198,660$ ;  $\nu_{MII}/R=1.8387$ ;  $\nu_{MIII}/R=1.8104$ ;  $\sqrt{\nu_{MII}/R}=1.3560$ ;  $\sqrt{\nu_{MIII}/R}=1.3455$ .

TABLE XVI

Calcium						
Int.	$\lambda$	$\nu$		Int.	$\lambda$	$\nu$
0	269.7	370769		0	727.4	137482
0	280.9	355973		0	732.9	136450
0	299.7	333712		0	736.3	135809
1	322.1	310492	O, Mg	1	740.2	135106
2	324.7	307939		0	745.9	134070
3	331.8	301414		0	748.2	133647
0	334.9	298570		1	773.7	129247
4	341.0	293290		0	800.1	124989
2	344.7	290141		0	810.1	123435
0	352.9	283382		0	821.2	121769
3	358.0	279314		0	846.5	118140
6	403.8	247672		1	856.5	116752
6	410.1	243837		0	875.3	114247
0	439.7	227412		0	883.0	113255
0	444.1	225164		0	934.6	106997
0	450.5	221956		0	1084.6	92198
0	477.5	209428		0	1286.7	77718
0	535.1	186881		0	1434.2	69724
3	537.8	185957	C <sub>2</sub>	0	1454.3	68763
1	542.2	184444		0	1464.1	68301
1	558.1	179176		0	1485.9	67299
0	572.0	174825		0D	1500.0	66668
1	600.9	166406	O <sub>1</sub> , C	5	1545.6	64700
0	629.0	158977	O <sub>1</sub>	5	1555.0	64307
0	632.7	158053		4	1562.4	64005
1	638.0	156747		0	1571.5	63635
0	642.5	155649	C	0	1586.1	63047
3	646.4	154708		0	1647.5	60700
0	651.0	153610	C	0	1807.8	55315
5	655.9	152465		0	1814.8	55103
4	669.6	149347		10D	1838.9	54382
0	688.6	145222				

Bohr and Coster,<sup>2</sup> who had no data sufficiently accurate to enable them to differentiate between the two levels, give the value of  $\nu/R$  for these levels as 2.0. Their probable error as may be seen from their series of values, is of the order of .5, so that our results are in complete agreement with preceding estimates of these levels and actually for the first time fix their values accurately.

The foregoing is the only certain success which has yet been reached in the fitting of the calcium spectrum into the Bohr theory, but the simplicity of the spectrum and the strength of the main lines make it an alluring one for further studies of this sort. The many faint lines are almost certainly, and some of the stronger very probably, due to the removal of more than one of the 8 electrons which are in the M shell of calcium.

TABLE XVII

*Chromium*

Int.	$\lambda$	$\nu$		Int.	$\lambda$	$\nu$	
1	202.6	493486		2D	585.1	170923	
1	207.2	482556		3	595.5	167920	
0	214.9	465441		2	599.5	166803	O <sub>2</sub>
0	222.6	449297	?	2	608.3	164398	O <sub>2</sub>
1	226.4	441677		5	613.8	162927	
0	231.7	431667	? O <sub>2</sub>	6	619.9	161324	
2	238.6	419182	O <sub>2</sub>	6	629.9	158763	
1	253.8	393964		5	634.0	157736	
1	263.1	380055		6	637.8	156796	
2	269.8	370617		1	643.5	155393	O <sub>2</sub>
0D	278.0	359777		4	648.7	154159	
0	294.9	339121	? O <sub>2</sub>	4	654.9	152704	
1	308.1	324570		3	661.0	151291	
1	322.0	310569	O <sub>2</sub>	5	667.1	149896	
1	328.4	304535	O <sub>2</sub>	3	673.4	148507	
3D	336.3	297345		4	677.6	147575	
0	345.3	289645	O <sub>2</sub>	5	681.3	146785	
2	352.2	283913		4	687.7	145423	
0	361.3	276775		5	694.7	143953	
1D	369.7	270482		3	706.1	141619	
1	378.1	264459		2	710.0	140837	
1	384.1	260362		3	712.6	140339	
0D	394.0	253807		1	724.6	138007	
0	402.2	248633		1	728.6	137242	
4	434.6	230118	O <sub>2</sub>	3	745.0	134225	
4	438.3	228149		2	749.7	133385	
4	456.8	218924		1	754.1	132608	
4	464.0	215499		4	764.4	130830	
4	469.8	212847		2	768.2	130171	
0	475.4	210362		3D	780.1	128192	
0	483.4	206864	?	3	786.0	127225	
0	487.7	205031	?	2	790.2	126555	
2	498.0	200803		2	796.2	125590	
2	508.0	196866	O <sub>2</sub>	1	803.6	124435	
2D	515.7	193930		2	808.9	123619	
2D	524.3	190749	O <sub>2</sub>	1	815.2	122668	
3D	531.1	188285		1	818.4	122193	
2D	540.0	185199	O <sub>2</sub>	0	825.3	121171	
1	547.0	182812		0	850.9	117525	
1	553.6	180646	O <sub>2</sub>	1	854.3	117049	
1	563.0	177620		0	877.5	113967	
5	575.3	173816					

## CHROMIUM AND COPPER

The spectra of chromium and copper obtained from the pure metals are shown in Tables XVII and XVIII. Plate II also gives the reproduction of the copper spectrum.

TABLE XVIII

*Copper*

Int.	$\lambda$	$\nu$	Int.	$\lambda$	$\nu$	
0	155.7	642426	1	426.1	234670	
0	159.4	627392	1	433.0	230942	
0	164.6	607718	1	438.9	227822	
0	169.7	589449	3	444.0	225240	
0	186.1	537403	4	446.6	223934	
0	189.2	528625	2	450.5	221985	
0	198.5	503804	7	452.8	220858	
0	200.6	498405	3	459.2	217761	
0	203.8	490653	5	464.3	215401	
0	207.2	482672	2	467.2	214037	
1	210.9	474203	3	472.5	211663	
0	215.5	464123	3	476.2	210005	
0	219.7	455083	1	481.9	207503	
0	235.4	424773	4	484.5	206411	
0	237.9	420433	4	491.8	203326	
0	241.9	413411	1	494.4	202278	
1	248.5	402447	3	496.9	201260	
1	252.9	395382	4	499.6	200176	
2	255.0	392126	8	505.4	197883	
1	259.1	385907	1	509.1	196413	
1	262.4	381112	0	513.7	194681	
1	268.8	371996	0	516.5	193611	
1	270.1	370247	0	521.0	191946	
0	272.6	366811	0	523.8	190916	
0	274.9	363782	0	526.9	189786	
0	278.6	358976	0	531.8	188048	
2	281.6	355151	0	536.8	186296	
1	283.6	352572	2	540.7	184952	
0	286.5	349065	2	542.4	184379	
0	297.2	336462	2	547.1	182795	
1	299.5	333890	2	548.5	182309	
1	304.2	328785	2	550.8	181551	
1	306.7	326052	1	553.1	180789	
1	310.1	322529	1	555.8	179914	
1	312.4	320061	1	559.5	178731	
6	324.5	308157	0	568.1	176041	
5	329.2	303739	1	573.1	174496	
4	333.2	300165	1	584.6	171054	
4	335.8	297796	0	588.4	169941	
3	339.8	294325	1	598.4	167118	
3	342.6	291903	1	602.7	165915	
3	345.4	289528	1	606.0	165014	
3	348.2	287175	0	609.4	164101	
3	350.5	285339	0	611.2	163613	
1	353.6	282821	2	615.8	162388	
1	355.3	281429	2	619.9	161311	
5	358.0	279298	0	623.1	160485	
4	361.0	277031	0	624.9	160038	
2	364.0	274725	0	642.3	155683	C <sub>s</sub>
1	367.0	272502	0	649.1	154057	
2	371.4	269244	0	657.6	152059	
1	374.7	266880	0	662.3	150998	
2	377.6	264816	1	666.4	150067	
3	379.3	263630	1	672.1	148790	
1	387.5	258098	3	676.5	147828	
2	405.9	246372	3	682.1	146600	
0	408.8	244630	3	687.6	145427	C <sub>s</sub>
0	411.2	243214	3	691.2	144672	
0	413.5	241834	1	693.0	144292	
1	418.1	239160	3	700.1	142841	
0	422.6	236636	1	712.2	140416	



*Copper (Cont'd)*

Int.	$\lambda$	$\nu$	Int.	$\lambda$	$\nu$	
3	715.3	139796	2	808.7	123663	
2	719.4	139014	2	813.3	122953	
1	723.6	138202	2	833.1	120028	O <sub>3</sub>
3	730.3	136934	2	836.0	119624	O <sub>3</sub>
2	731.9	136623	1	840.7	118948	
2	735.0	136049	2	844.4	118427	
2	743.4	134510	2	858.1	116541	C <sub>3</sub>
0	750.7	133214	1	868.8	115101	
0	753.9	132640	2	872.3	114639	
1	758.6	131830	2	875.1	114271	
0	767.4	130312	2	878.4	113842	
5	777.3	128657	1	884.2	113097	
6	788.3	126860	1	887.3	112703	
4	791.4	126354	1	890.2	112338	
2	792.8	126138	2	893.8	111883	
2	797.5	125400	1	896.7	111521	
3	801.0	124849	2	900.1	111102	
3	803.2	124504				

It will be noticed that the copper extends on our plates down to 155 Å the four lines of lowest wave-length appearing very definitely and exactly measurably on both sides of the central image. Since the  $M_{II} M_{III}$  levels of copper as computed by Bohr and Coster and Sommerfeld from x-ray measurements in the K series (K absorption edge and  $K_{\beta}$  line) are at 175 Å, according to Bohr, and 186 Å according to Sommerfeld, while our observed lines run down to 155 Å, it is clear that our plates show practically the complete M spectrum, including the jumps to the  $M_I$  level, which is of course somewhat farther down in wave-length than the  $M_{II} M_{III}$  levels.

The same is of course true in the case of chromium whose  $M_{II} M_{III}$  levels are predicted by Bohr and Sommerfeld at 260 Å and 276 Å respectively while our chromium lines go down to 202.6 Å.

*This means that our method is capable of revealing the full M spectra of all the elements up to copper (atomic number 29) and that we have observed them all save for a few omissions above 20.* It is interesting that the crystal spectrometer is at present capable of going down to the same point, copper, in the L series.

Copper is furthermore the first element in which the M levels are all full.<sup>2</sup> The fact that its M spectrum consists of an enormous number of lines extending from 155 Å clear up to the visible (our plates themselves stop at about 900 Å merely because of the way in which they happened to be taken) indicates that many of its 18 M electrons are removed in our sparks, each one of them giving rise to its characteristic series of lines. Since it is the first element in which the M shell is full the M electrons may be expected to be very lightly held.

## THE PROGRESSION OF SPECTRA WITH ATOMIC NUMBER

Plates I, II, III and IV all reveal directly a progression of spectra with atomic number in this ultra-violet region which is quite like the progression discovered by Moseley in the hard x-ray region.

Plate I for example, the magnification in which is about 2 fold, shows the most powerful line in each of the L spectra of the elements from boron to fluorine progressing systematically toward shorter and shorter wavelengths as indicated by the arrows. In the case of boron the strongest line is just off the plate; in the case of carbon that line is undoubtedly at 1335.0 Å. In the case of nitrogen it is at 1085.2 Å, in oxygen it is unquestionable at 834.0 Å, in fluorine it is 656.4 Å (other fluorine plates bring this out much more sharply than does the one here given which was preferred for other reasons.) Each spectrum has in general few if any strong lines of longer wave-length than this line of maximum intensity.

Plate II, the magnification of which is about 10 fold, shows the same sort of progression of the L spectra of sodium, magnesium and aluminum.

Plate III, of magnification about 2, illustrates very satisfactorily the progression of the M series through magnesium, aluminum, silicon, phosphorus, sulphur and chlorine.

Plate IV, of magnification 3.5, reveals beautifully the progression of the M series through phosphorus, sulphur, chlorine, potassium and calcium even though this series of elements runs right through argon which should come in between chlorine and potassium.

When Moseley brought to light such a progression in the hard x-ray field, he plotted merely the square root of the frequency of the strongest observed lines to obtain his relation between frequency and atomic number. If we adopt the same procedure arbitrarily calling this line  $L\alpha$  in conformity with the convention which one of us previously adopted,<sup>1</sup> we obtain a spectroscopic progression (see Fig. 2) which in the case of both the K and the L series is complete from hydrogen to uranium barring only a few short gaps. These gaps, however, are in straight portions of the curves and hence intermediate points can be accurately determined by interpolation.

In this plotting there is in general no ambiguity about which line to call the strongest line. In sodium, for example there is but one certain line of the L series and this corresponds to the lowest permissible energy jump into the  $L_I$  level. In the case of magnesium and of aluminum there are two lines of intensities quite comparable, and we have taken in each case the one of these which corresponds, as in the case of sodium, to the lowest energy jump to the  $L_I$  level. Similarly for neon, upon which we

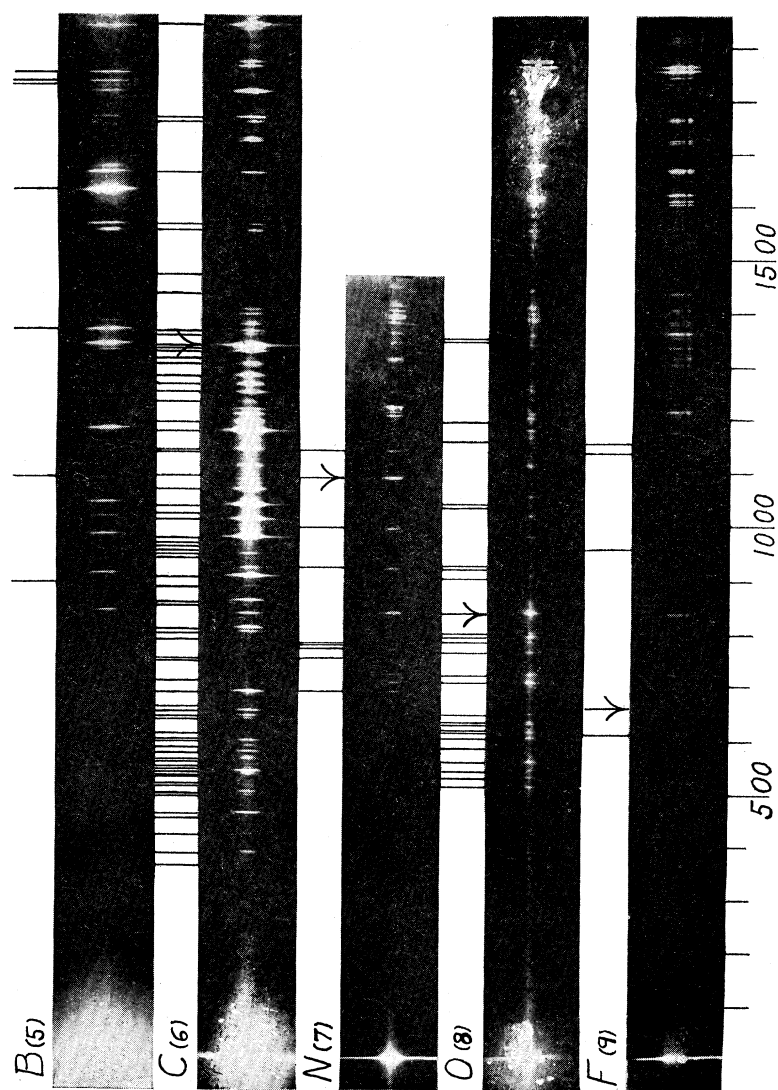


PLATE I. Spectra of boron, carbon, nitrogen, oxygen and fluorine.

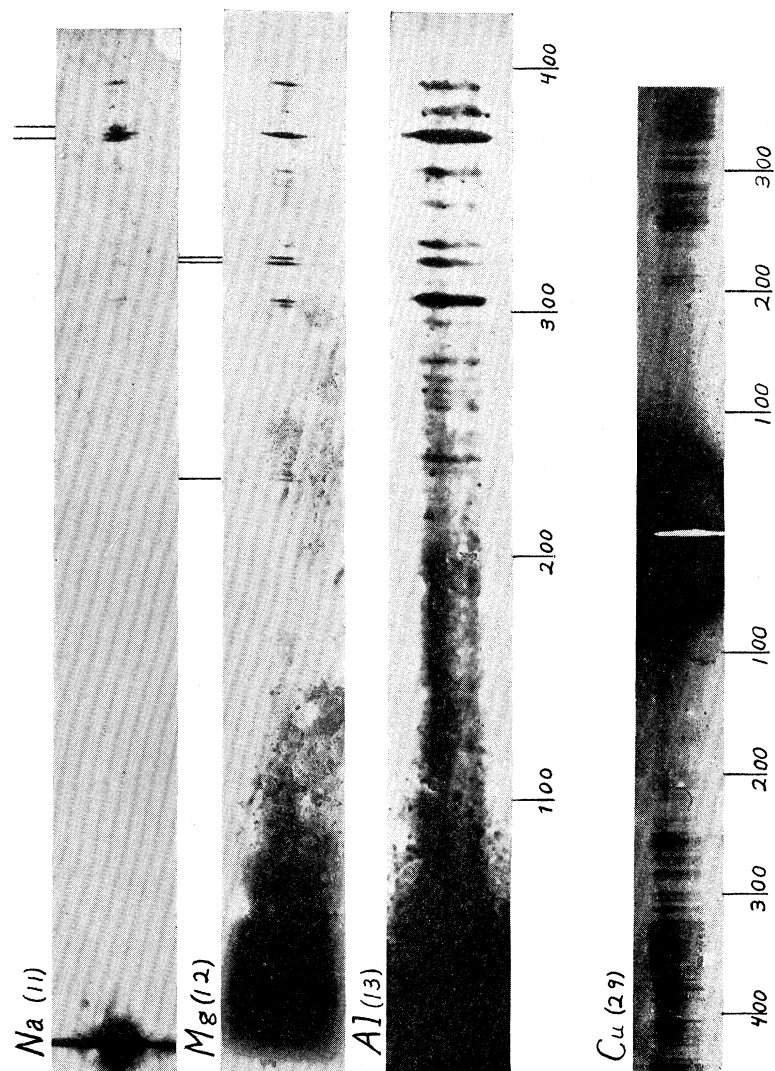


PLATE II. Spectra of sodium, magnesium, aluminum and copper.



PLATE III. Spectra of magnesium, aluminium, silicon, phosphorus, sulfur and chlorine.

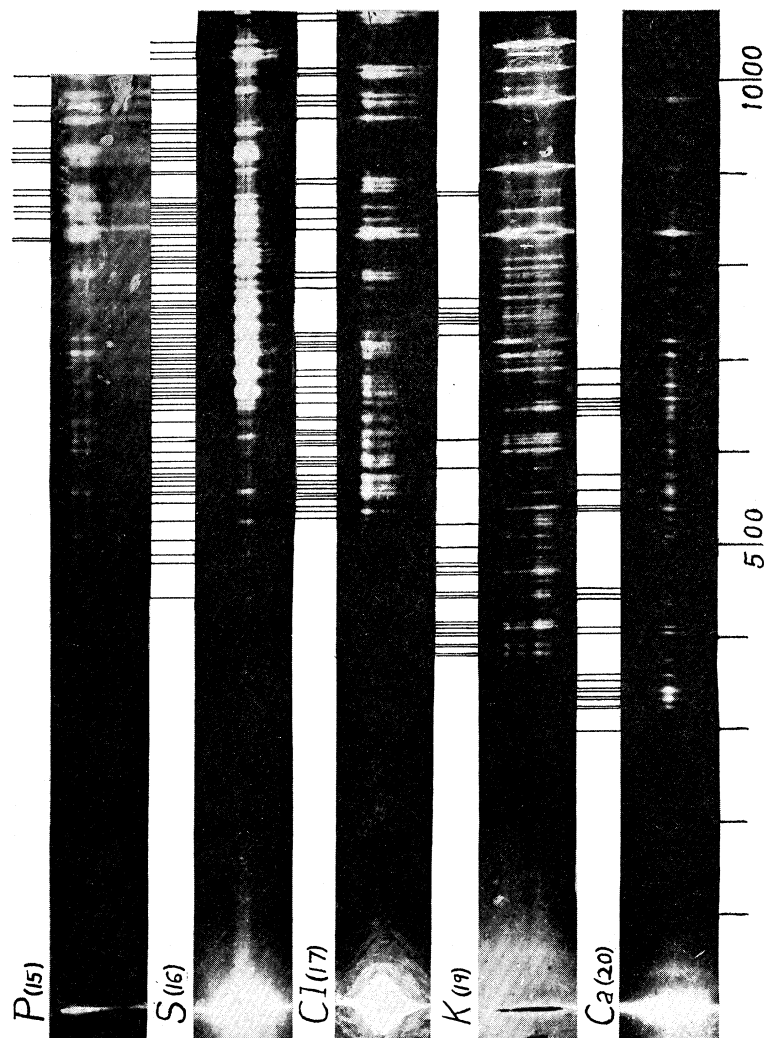


PLATE IV. Spectra of phosphorus, sulfur, chlorine, potassium and calcium.

have made no measurements ourselves, we have plotted that one of the Horton and Davies radiation potentials which should correspond to this jump, namely that at 17.8 volts,  $\nu = 144180$ .

These remarks illustrate the fact that there is no completely consistent way of carrying through a Moseley progression so long as we attempt to plot any particular line, a fact brought to light quite sharply by the observation that there appears on our plates no  $L_{II} L_{III}$  doublet in sodium, for example, at all. We have thought it worth while, however, to retain Fig. 1 for the sake of exhibiting in a general way the progression of spectra throughout the whole range of the elements, a result which for the present can be best attained by plotting merely the strongest line of the L series, a line which we have arbitrarily called  $L\alpha$ , without, however, implying any relationship to any of the confused conventions now in use by various authors in the designation of particular lines as  $\alpha_1$ ,  $\alpha_2$ ,  $\alpha_3$ ,  $\beta_1$ , etc.

The ultimate exhibition of spectral progression will be through the plotting of levels or absorption edges rather than of lines and our Fig. 1 extends this type of relationship already used by Bohr and Sommerfeld to a group of elements for which these have not before been accurately known, but no completeness of progression through the elements is yet possible in this way.

#### ATOMS STRIPPED OF ALL VALENCE ELECTRONS

The recent work of Paschen and Fowler in definitely working out the series corresponding to Al(III) and Si(IV) and the evidence presented above that the lines of these series appear with extraordinary intensity in our sparks makes it highly probable that in the elements from lithium to fluorine also, all of the valence electrons are frequently stripped from the atom, for exactly the same causes must operate in the two cases. This inference is somewhat strengthened by the regular progression of the very intense line which we have called the  $L\alpha$  line in going from lithium to fluorine. In lithium there is but one valence electron and the strongest lithium line is here definitely known to be due to the jump of this electron to the position of minimum energy from the next lowest energy level. It is this "hydrogen-like" spectrum which we are here designating as the spectrum due to the atom stripped of valence electrons. It is in fact the spectrum due to one single electron moving between the series of levels characteristic of a nucleus of unchanging charge which holds a single electron in its influence. This series of lines is of course the same so far as wave-length is concerned whether that electron has been entirely

removed and is at the observed instant giving off radiations because it is returning from infinity by jumps to its most stable orbit, or whether it has never left the atom but has simply been displaced from this most stable orbit to one or another of its possible states of higher potential energy. This latter case would correspond indeed to a larger intensity of the longest wave-length line of the series and is perhaps more likely to represent the actual behavior of the electron in the production of the spectra which we are considering, but for the sake of having a single notation to represent this series of wave-lengths alone we are here designating both cases as the spectrum due to an atom stripped of its valence electrons.

In the case of beryllium by far the strongest lines in the spectrum of our sparks, taken in the optical region with the quartz spectrograph, is the pair at 3130.55 Å and at 3131.19 Å which is definitely known to be due to the "stripped atom" i.e. to ionized beryllium.<sup>14</sup>

The strongest line on our plates due to boron is a very powerful pair at 2066.2 and 2064.2 Å. This pair is reported by Eder and Valenta as a very weak "spark line." That it is by far the strongest line on our plates, which in general also show the highly ionized lines like those of Al(III), Si(IV), P(V), etc., in extraordinary strength is evidence in itself that this line is due to B(III), i.e., to the stripped boron atom.

If then the strongest lithium, beryllium and boron lines are all due to stripped atoms, the unmistakable progression between these lines and the most powerful line in each of carbon, nitrogen and oxygen, points to the conclusion that this line which we have called  $L\alpha$  in all these substances is due to "stripped" atoms, for such progression is to be expected among "hydrogen-like" atoms of continually increasing nuclear charge.

This evidence is further supported by the similarity in character of these lines which we have called  $L\alpha$  lines. If these lines are all due to "stripped" atoms they should all be doublets, since the strongest line in all "hydrogen-like"\* spectra is a doublet, and the value of  $\Delta\nu$  for these doublets should increase systematically with increase in atomic number. Thus in the M series we now have definite knowledge not only of the existence of this characteristic doublet in the spectra of the "stripped" atoms of the elements from sodium to phosphorus, but the following table shows the progression in the frequency separation (in  $\text{cm}^{-1}$ ) of this doublet, the

<sup>14</sup> Paschen-Gotze, *Serien Gesetze der Linien Spectrum*, p. 71.

\*This term is used following Sommerfeld to designate spectra due to but one valence electron.



data on Al(III) and Si(IV) being taken from the papers of Fowler and Paschen while the separation of the phosphorus doublet is taken from our own plates.

	Na(I)	Mg(II)	Al(III)	Si(IV)	P(V)
$\Delta\nu =$	17	92	238	460	795

Now in the case of lithium and beryllium the line which we have called  $L\alpha$  is without any ambiguity a doublet due to a "stripped" atom. In the case of boron, in view of the Sommerfeld law of the alternation of doublets and triplets in going across the periodic table, the only possible doublets due to boron must be, first, an arc doublet in the spectrum of B(I), and, second, a spark doublet in B(III). Our doublet at 2064 Å is definitely a spark line, and furthermore it has not the separation of the arc doublet. Hence it must be due to a "stripped" boron atom.

Again, for the reason just given, carbon can have doublets only in C(II) and C(IV). Our  $L\alpha$  line at 1335.0 has now been definitely measured as a doublet by both Simeon<sup>15</sup> and Hopfield<sup>16</sup> with the average separation given in  $\text{cm}^{-1}$  in the following table.

	Li(I)	Be(II)	B(III)	C(IV)
$\Delta\nu =$	.34	6.6	47	67

It is the progression in separation and in wave-length which must be depended upon for the evidence that this is actually due to C(IV) rather than to C(II). The evidence for stripped atoms up to and including carbon is then exceedingly strong.

When the foregoing was written we felt that we were probably justified in inferring stripped atoms also in the case of nitrogen, oxygen and fluorine, especially since Lyman had reported both the line at 834.0 Å and that at 1085 Å as doublets. Hopfield and Leifson's<sup>16</sup> recent finding that these two lines were both triplets was, however, definitely in conflict with our inference, since if these lines were due to stripped O and N atoms they would of necessity be doublets. Accordingly we have just taken new plates using a very narrow slit (.02 mm) and obtaining very satisfactory spectra of these lines in both the third and fourth orders. The evidence of these plates is conclusive that both of these lines have a more complicated structure than that of a doublet, 834.0 showing clearly

<sup>15</sup> Simeon, Roy. Soc. Proc. **102**, 488, 1923

<sup>16</sup> Hopfield, Astrophys. J. **53**, 62, 1923

*seven* components and 1035 showing four. *This is conclusive evidence that these two lines are not due to stripped atoms.*<sup>17</sup>

NORMAN BRIDGE LABORATORY OF PHYSICS,  
CALIFORNIA INSTITUTE OF TECHNOLOGY,  
PASADENA, CALIFORNIA,  
September 15, 1923.

<sup>17</sup> This paragraph added January 12, 1924.

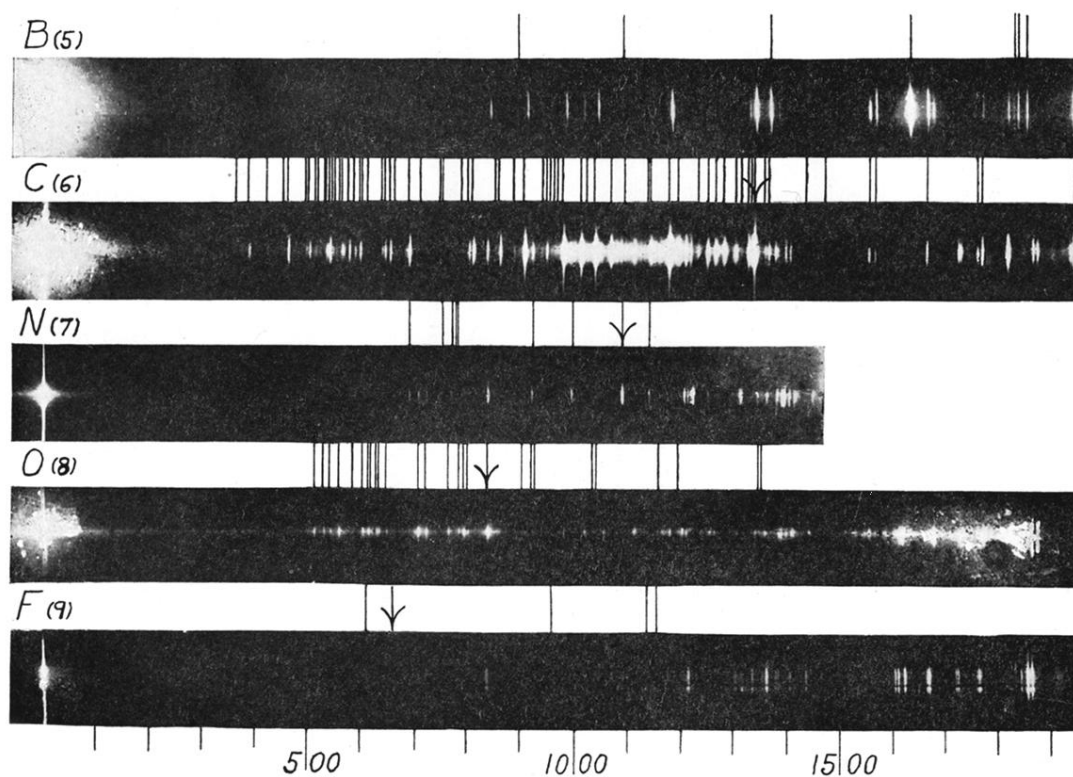


PLATE I. Spectra of boron, carbon, nitrogen, oxygen and fluorine.

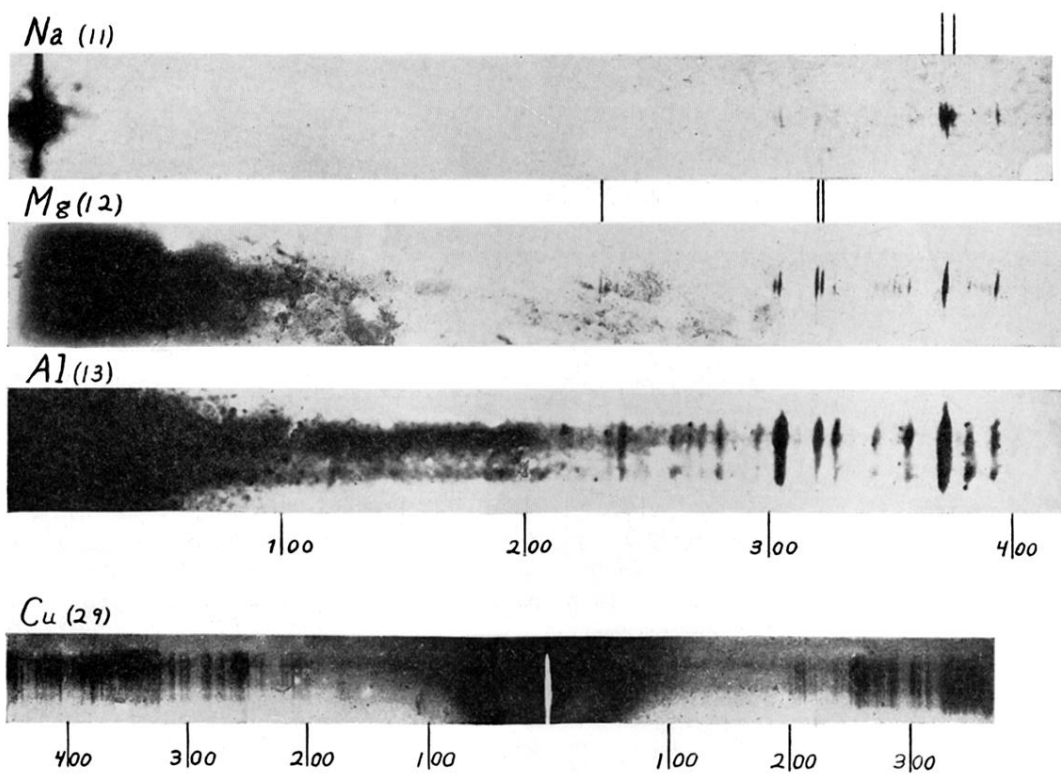


PLATE II. Spectra of sodium, magnesium, aluminium and copper.

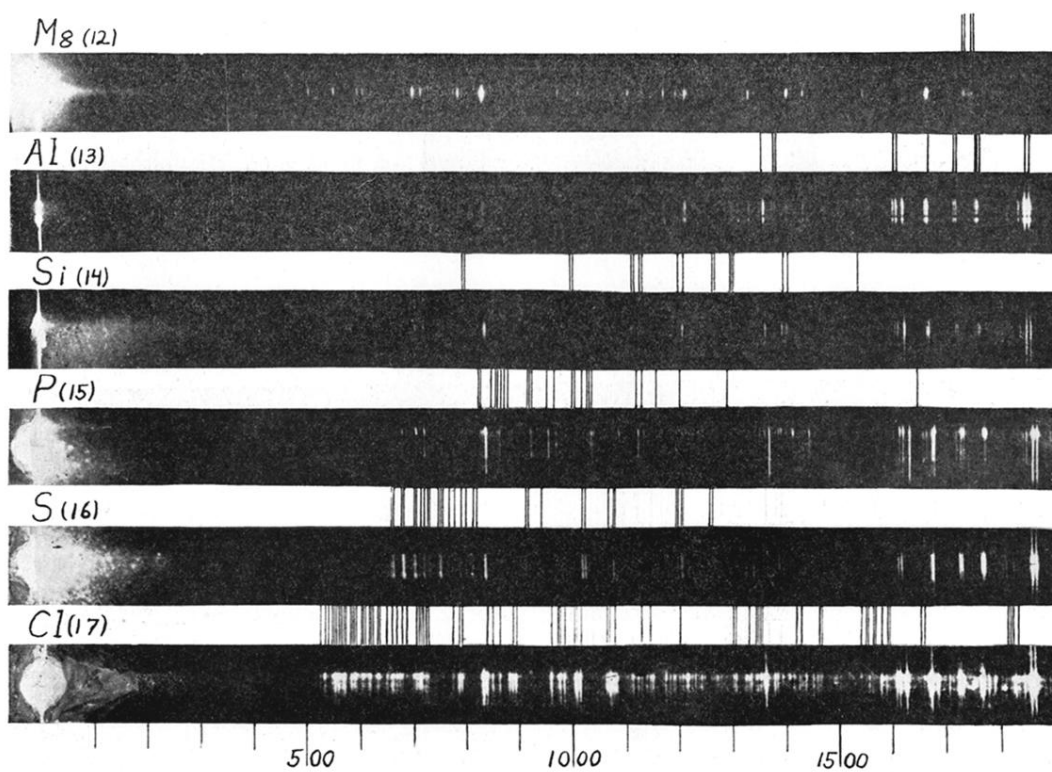


PLATE III. Spectra of magnesium, aluminium, silicon, phosphorus, sulfur and chlorine.

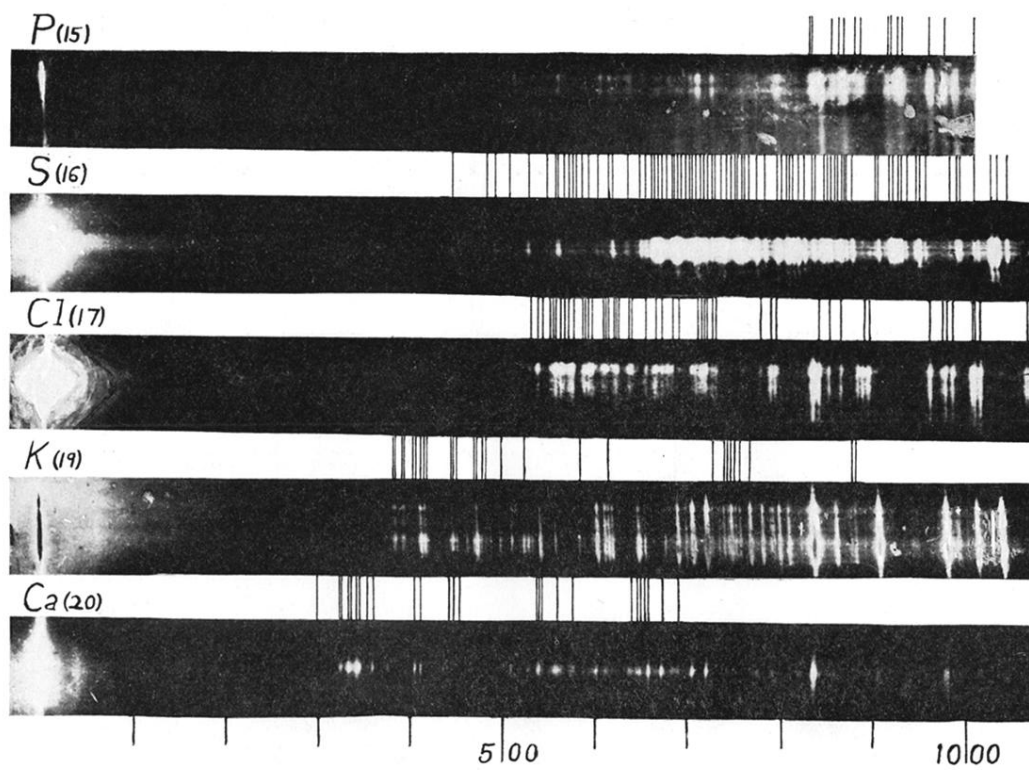


PLATE IV. Spectra of phosphorus, sulfur, chlorine, potassium and calcium.